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Understanding the Composition and Structure of Crystallographically Challenged Materials

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Amorphous or poorly crystalline materials are ubiquitous in the environment, where they are important actors in several chemical cycles, including H_2O , S, CO_2 , etc. Technologically, the utility of amorphous materials ranges from applications such as glass formation, for nuclear waste disposal for example, to biologically mediated nanoparticle formation and cryobiological research on organ preservation. The atomic arrangements in these materials, and the changes these arrangements undergo with changing environmental conditions, are key to understanding fundamental issues such as how such materials are stabilized in or destabilized from their nanocrystalline form. The derivation of useful models for atomic arrangements using the pair distribution function (PDF) approach are now well established; this maturity is the result of burgeoning capabilities at high-energy X-ray scattering beamlines and the judicious use of isotopically substituted materials at neutron sources. Further, there is growing realization that *in situ* studies are essential to ensuring the structures determined from PDF are useful and that metastable intermediate states are captured.

Several topical examples will serve to illustrate the need for complementary techniques to supplement PDF data. For example, a growing body of evidence confirms a single-phase model (SPM) suffices to explain the atomic arrangement in inorganically and biologically derived 2- and 6-line varieties of ferrihydrite, an important iron oxide hydroxide in environmental remediation applications. The 50 years of effort expended on studying this material produced inconsistent results, probably due to variations in preparation, and confusion due to over-fitting information-poor diffraction and X-ray absorption data with overly complex models. Careful large-batch synthesis of hydrogenous and deuterated samples and the use of several analytical probes, including IR, thermal analysis, and X-ray and neutron scattering on synthetic and natural samples now provide a consistent picture: (1) there is no need to fit the data with a three-phase model; and (2) models claiming water contents of 10% or more are at odds with combined *in situ* X-ray diffraction–differential scanning calorimetry (DSC) data and *ex situ* thermogravimetric analysis–DSC data.

X-ray measurements performed on glasses and aerodynamically levitated melt droplets show evidence of structural heterogeneities in the liquid state and the transitions in the glass state under compression. Changes in the PDF upon cooling or compression are enhanced using diffraction isosbestic points (DIPs) and the complementary use of ultrasonic techniques to reveal “hidden” transitions. For example, molecular dynamics simulations of CaO-SiO_2 melts and observations of DIPs indicate an underlying structure associated with the polymerization of CaO_6 units. In the high temperature liquid, DIPs indicate the increase in edge shared Ca octahedra is linear, however as the T_g is approached the magnitude of the structural changes increases rapidly.

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